Electrochemical Time-of-Flight Investigations of the Diffusion Processes in Complex 2D and 3D Molecular Systems

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Electrochemical time-of-flight (ETOF) methods are being developed to investigate dynamics of proton diffusion in complex vesicular systems and to probe diffusion processes in 2D systems of Langmuir monolayer films at the air/water interface.

Proton transport across and along inner mitochondrial membrane is one of the key mechanistic elements of the chemiosmotic energy transduction. We want to understand how the dynamics of proton diffusion is effected by proximity of the interfacial region of a phospholipid bilayer membrane. We are interested in mechanistic details and in measuring rates of vectorial proton transport along such interfaces relative to proton diffusion in bulk water. The 2D ETOF techqniques were also used to measure lateral mobility of redox active amphiphiles and lateral electron hopping in monolayer films of osmium diphenylphenanthroline perchlorate on the water surface [1].

Photolithographically fabricated generator-collector ETOF devices featured two parallel gold micro-electrodes (typically 7 mm in length, 40 μm wide, spaced by a 10 μm gap). In 2D ETOF measurements, such a device is touching the water surface where the generator and collector electrodes function as a collinear pair of line micro-electrodes. Bulk measurements, with a generator-collector device submerged in an electrolyte solution, were carried out to calibrate the devices by relating the transit times to the known D values of $Ru(NH_3)_6^{2+}$ in a series of solutions of different viscosity adjusted with sucrose. A new method to define and to measure transit times in the step mode ETOF experiments was developed that requires only the pseudo-steady-state values of the collector current.

Reliability of the 2D ETOF technique was established by investigating lateral diffusion of an amphiphilic tetradecane TEMPO derivative for which the D values were also measured by 2D voltammetry [2]. Combination of 2D ETOF and 2D voltammetry allows us to independently measure diffusion coefficients and concentrations of redox species. This advantageous feature was then used to reopen our previous investigations of the kinetics of lateral electron hopping in $Os(DPP)_3(ClO_4)_2$ (DPP is 4,7-diphenyl-phenanthroline) solid monolayers on the water surface [3]. The true rate constant of electron self-exchange, $k_{ex} = 1.0 \times 10^9\ M^{-1}s^{-1}$ was obtained. The fact that the latter is more than an order of magnitude larger than its value obtained in a homogeneous acetonitrile solution suggests that the structure and local of the $Os(DPP)_3^{III+/II+}$ monolayer system result in a larger electronic coupling and/or smaller reorganization energy.

Electrochemical proton time-of-flight is an analogous technique. Generation of protons is accomplished by electro-oxidation of hydrogen at a Pd(H) generator micro-electrode. The latter is fabricated by electroplating ca 300 atomic layers of Pd on the micro-fabricated gold substrate. While in this case the rate of proton generation is a kinetically controlled process, a quasi-steady-state conditions similar to those prevailing in the $Ru(NH_3)_6^{2+}$ experiments can be established. Measurements of the proton diffusive transients can be done either potentiometrically or amperometrically. In either case, a Pd overcoated collector microelectrodes are used. Relative advantages of these two approaches will be discussed as the applications of this novel technique to the measurements of proton mobilities in biological membrane systems are presented.

References

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